

## **An Introduction to Chapter 16: “Methods for Estimating Air Emissions from Chemical Manufacturing Facilities”**

John Allen Hatfield  
Mitchell Scientific, Inc.  
PO Box 2605  
Westfield, NJ 07091-2605  
[aHatfield@MitchellScientific.com](mailto:aHatfield@MitchellScientific.com)

### **Abstract**

Chemical processing plays an integral part in most manufacturing operations. While the purpose of each industry is to meet different manufacturing objectives, most chemical processes include at least one or more of the four common operations: preassembly, reaction, isolation, and purification. Process operations may be continuous in nature and operate for long periods of time or they may consist of many discrete events and operate in a batch wise fashion.

Measuring the air emissions from a boiler or other combustion operation is largely accomplished through stack sampling and analysis. However, assessing the air emissions that occur from a chemical process is much more involved since the process takes place at different intervals throughout the manufacturing operation. The emissions that occur during a combustion operation are fairly predictable and largely dependent upon the fuel that is being used and the boiler performance. Emissions that occur during a chemical process depend upon the solvents that are used, the chemicals that required as well as the specific types of unit operations that are followed.

Having established calculation procedures that can be applied to all chemical processes without regard to industry is important because it standardizes the environmental analysis while at the same time normalizes environmental regulations. The purpose of this document is to review many of the air emission calculation models that are contained in EIIP Document *Chapter 16: Methods for Estimating Air Emissions from Chemical Manufacturing Facilities*, August 2007.

## INTRODUCTION

Chemical processes vary not only across different industries but also within the same industry. Each process is governed by a specific chemical pathway and the required unit operations to meet primary production objectives. However, when one examines several processes across many industries then it is easy to see that they all share certain common features. Most chemical processes include at least one or more of four basic operations: preassembly, reaction, isolation, and purification. For example, a chemical process that produces a final product from raw materials would most likely include a preassembly step (where raw materials are combined in the presence solvents), a reaction step (where different raw materials react through the designed chemistry), and isolation step (where product is separated from process streams), and a purification step (where process impurities are removed from the final product). A solvent recovery operation would include an isolation step (where the pure solvent is separated from the spent process solvent) and/or a purification step (where the solvent quality is further refined).

From the perspective of air emissions calculations, most processes can be modeled using one or more of seven basic air emission equation models. These models include but are not limited to filling, gas sweep, vacuum operation, gas evolution, empty vessel purge, depressurization, and heating. These key equation models along with many worked illustrations are presented in *Chapter 16: Methods for Estimating Air Emissions from Chemical Manufacturing Facilities*. A recent addition to the Chapter 16 manuscript was a completely new section pertaining to the emission calculations for single stage vent devices such as vent condensers, vacuum pumps, and vacuum steam jets. The final document was published in August 2007. The purpose of this article is to provide a brief overview of many of the key topics and equations that are contained in the Chapter 16 document.

## BODY

### Ideal Gas Law Models

#### Filling and process transfer operations.

Filling and process transfer operations are perhaps the most widely used processing procedures followed in industry. Filling is used when the chemical operator must place different raw materials, process intermediates, and solvents into a vessel in preparation for a chemical reaction. Once the reaction is complete then the batch must typically be transfer to the next vessel where water or a different process solvent might be charged as part of an extraction operation.

Every time solids or liquids enter the process vessel, noncondensable gases and solvent vapors contained in the headspace of the vessel at the time must exit. It is this aspect of the charge or transfer operation that leads to air emissions from the process vent. The volume of process material that enters the vessel is generally equal to the volume of gas that is displaced from the vessel headspace. The total moles of gas that are emitted from a displacement operation can be calculated using the ideal gas law as follows:

$$\text{Equation (1): } E_n = \frac{PV}{RT}$$

Where

$E_n$  are the moles of gas that are displaced by the filling operation  
 $P$  is the system pressure of the vessel headspace  
 $V$  is the displacement volume  
 $T$  is the temperature of the gas that is exiting the vessel  
 $R$  is the universal gas constant

The vapor composition in the headspace is another important factor when considering air emissions from filling operations. Raoult's Law may be used in conjunction with activity coefficients to estimate the component vapor pressures in the headspace from the batch composition as shown in Equation (2).

$$\text{Equation (2): } p_i = x_i \gamma_i P_i$$

Where

$p_i$  is the partial pressure of liquid component  $i$   
 $x_i$  is the mole fraction of component  $i$  in the liquid  
 $\gamma_i$  is the activity coefficient of component  $i$  in the liquid  
 $P_i$  is the pure component vapor pressure of component  $i$ .

Finally, Equation (1) and Equation (2) can be combined in Equation (3) to calculate the moles of each volatile component that are emitted from a vessel from a filling operation.

$$\text{Equation (3): } n_i = \frac{p_i V}{RT}$$

Where

$n_i$  are the moles of component  $i$  that are emitted

Assuming that the vessel is empty prior to the start of the filling operation, then these equations may be used to calculate the emission quantity of each component in the vessel headspace.

Complicating factors arise when the vessel already contains process material of the different composition at the start of the filling operation. If the filling operation takes place by way of subsurface addition (where the inlet stream enters the vessel below the surface of the batch) then a set of dilution factors can be calculated for estimating the average batch composition to use for Equation (2). On the other hand, if the filling operation takes place in an above surface fashion (where the inlet stream enters the vessel through an upper port and falls freely into the batch through the vessel headspace) then one would need to compare the component vapor pressures of the inlet stream to those based on the average batch composition (using dilution factors) and take the greater component vapor pressure to use in Equation (3). The reader is referred to the Chapter 16 document where mixing dilution factors are more fully described.

## Partial Pressure Ratio Models

The ideal gas law plays a major role in most of the emission calculation models. Given components A and B in the gas form the following ideal gas law relationships can be written:

$$\text{Equation (4): } n_A = \frac{p_A V}{RT} \qquad n_B = \frac{p_B V}{RT}$$

Where

$n_A, n_B$  = moles of component A and B in the gas form,  
 $p_A, p_B$  = partial pressure of component A and B,  
 $V$  = gas space volume,  
 $R$  = ideal gas constant in consistent units,  
 $T$  = is the temperature of the system.

Both expressions in Equation (4) can be combined and rearranged to show that the ratio of the moles of component A and B is equal to the ratio of the partial pressures.

$$\text{Equation (5): } \frac{n_A}{n_B} = \frac{p_A V / RT}{p_B V / RT} \quad \Rightarrow \quad \frac{n_A}{n_B} = \frac{p_A}{p_B}$$

Finally, Equation (5) can be rearranged to show that the moles of component A can be calculated from the moles of component B and the ratio of the two partial pressures as shown in Equation (6).

$$\text{Equation (6): } n_A = n_B \frac{p_A}{p_B}$$

Equation (6) is used repeatedly throughout Chapter 16 in many of the models as a means of calculating the moles of condensable component  $i$  from the moles of the noncondensable component (air, nitrogen, ...) and the ratio of the two partial pressures as shown in Equation (7).

$$\text{Equation (7): } n_i = n_{nc} \frac{p_i}{p_{nc}}$$

Where

$n_i$  = moles of condensable component  $i$  leaving the process,  
 $n_{nc}$  = moles of noncondensable gas leaving the process,  
 $p_i$  = partial pressure of component  $i$ ,  
 $p_{nc}$  = partial pressure of the noncondensable component.

## Gas Sweep

The use of a noncondensable gas in chemical processing is a very common practice. For example, nitrogen is used for safety reasons to inert the headspace when the vessel contains a highly flammable solvent. At other times, a nitrogen sweep is used to prevent moist air from entering the vessel and causing chemical impurities to form in the batch due to the presence of moisture in the process. Under a

different scenario, large amounts of air can sweep across the batch liquid surface as solids are being charged into the vessel and a strong suction exists at the vent discharge.

At times when the vessel contains volatile solvents and a nitrogen gas sweep is used to inert the vessel or to prevent moisture from entering into the process then a different approach is used to calculate the solvent emissions from the operation. In most chemical processes, the nitrogen flow rate is sufficiently low that one can assume that the exit gas from the vessel is completely saturated with solvent vapors from the batch. This would certainly be the case in the pharmaceutical industry where high chemical purity is critically important. It would also be the case in other industries where process reactors and other conventional equipment are involved in the process.

However, in certain industries such as paint manufacturing there can exist large dispersion vessels with flat covers featuring large solids charge chutes and a retractable agitator assembly system. A ventilation system for this type of process operation can impart a large air sweep across the liquid surface. The assumption that the exit gas is fully saturated when the gas sweep rate is high is not valid. Under high gas sweep conditions the liquid solvent is unable to evaporate and diffuse away from the liquid surface fast enough to maintain saturated conditions. Equation (8) is the basic relationship that is used to calculate the solvent vapor emission rate based on the condensable gas sweep rate, the vapor pressure of the solvent, and the solvent vapor saturation level. Equation (8) is an implementation of Equation (7). Detail procedures for calculating the saturation factor ( $S_i$ ) are discussed Chapter 16.

$$\text{Equation (8): } E_{R-i} = E_{R-nc} \frac{p_i}{p_{nc}} = E_{R-nc} S_i \frac{p_i^{sat}}{p_{nc}^{sat}}$$

Where

$E_{R-i}$  is the molar flow rate of solvent component  $i$  being emitted,

$p_i^{sat}$  is the saturated vapor pressure of component  $i$ ,

$p_{nc}^{sat}$  is the saturated partial pressure of the noncondensable gas (i.e. air, nitrogen) at saturated solvent conditions.

### **Vacuum Operations**

Several process operations are carried out under vacuum conditions. For example, it is not uncommon for a batch or continuous distillation to be performed at reduced pressure as a means of operating at a below normal boiling temperature of the batch. Vacuum pumps and/or steam jets are connected to the process vent and are used for maintaining the desired vacuum level. When a vessel containing a volume of solvent liquid is placed under vacuum for long periods of time then air will leak into the process at the flanges and fittings. Air that leaks into system comes in contact with the solvent before finally exiting the vessel through the vent to the vacuum pump.

The solvent emissions that occur from vacuum operations is calculated in a similar manner as the standard gas sweep model for a partially filled vessel assuming 100% saturation. Air leaving the system is considered to be the noncondensable gas component and the moles of solvent vapor that is emitted from the vessel is calculated by the ratio of the partial pressure of the solvent vapor to the partial pressure of the air. The ideal gas law relations from Equation (7) are applied to Vacuum Operations as shown in Equation (9).

$$\text{Equation (9): } E_{R-i} = E_{R-nc} \frac{p_i}{p_{nc}}$$

Where

$E_{R-i}$  is the molar flow rate of solvent component i being emitted,

$E_{R-nc}$  is the molar flow rate of the noncondensable component being removed from the system,

$p_i$  is the vapor pressure of component i,

$p_{nc}$  is the partial pressure of the noncondensable gas (i.e. air, nitrogen).

### **Gas Evolution**

Solvent emissions that occur during a chemical reaction when one or more gases are generated can be calculated similarly to the gas sweep and the vacuum operation models. In the Gas Evolution model, gas that is generated by the reaction is considered to be the noncondensable component which is saturated with solvent vapors as it exits the reactor. This is shown in Equation (10).

$$\text{Equation (10): } E_{R-i} = E_{R-rxn} \frac{p_i}{p_{rxn}}$$

Where

$E_{R-i}$  is the molar flow rate of solvent component i being emitted,

$E_{R-rxn}$  is the molar flow rate of the reaction off gas leaving the system,

$p_i$  is the vapor pressure of component i,

$p_{rxn}$  is the partial pressure of the reaction off gas (i.e. HCl, SO<sub>2</sub>, N<sub>2</sub>).

### **Emission Models Due to Dynamically Changing Process Conditions**

When system conditions change such as the pressure becomes less or the temperature becomes greater then emissions will occur from the process. The mathematics that relates changing process conditions to the emission are more complicated than the preceding ideal gas law models.

### **Empty Vessel Purge**

When a vessel becomes empty after the batch has been transferred to another vessel, then nitrogen is often used to displace the remaining solvent vapors left behind by the process. In this case, the initial amount of solvent vapor that is contained in the empty vessel at the beginning of the empty vessel purge can be calculated using the known partial pressure of the solvent vapor and the ideal gas law. However, as the empty vessel continues to undergo a purge and vapors leave the vessel then the remaining solvent vapor concentration becomes less and less over time. The net emission of solvent vapor from the vessel can be calculated using Equation (11).

$$\text{Equation (11): } E_{n-i} = \frac{P_{i,1}V}{RT} \left( 1 - e^{-Ft/V} \right)$$

Where

$E_{n-i}$  are the moles of component i that are emitted from displacement,  
 $P_{i,1}$  is the saturated vapor pressure of component ii at initial conditions,  
 $V$  is the gas space volume of the vessel when empty,  
 $R$  is the ideal gas constant in consistent units,  
 $T$  is the temperature of the liquid being charged,  
 $F$  is the purge gas flow rate,  
 $T$  is the elapsed time for the purge operation.

### **Depressurization Operations**

When a vacuum pump is used to reduce the operating pressure of a process vessel (containing solvent) from atmospheric pressure down to the desired vacuum level then emissions will occur through the vacuum vent. As the pressure falls from its initial level down to the target level, solvent liquid in the vessel evaporates as it must maintain saturated vapor pressure conditions. Therefore, the partial pressure of the solvent is considered to maintain a constant value since the operation is generally isothermal and the partial pressure of the noncondensable gas becomes less in conjunction with system pressure. The moles of solvent vapor that are emitted from a depressurization operation are calculated using Equation (12).

$$\text{Equation (12): } n_{i,out} = \frac{Vp_i}{RT} \ln \left( \frac{P_{nc,1}}{P_{nc,2}} \right)$$

Where

$n_{i,out}$  = moles of volatile component i leaving the vessel,  
 $p_i$  = vapor pressure of component i,  
 $P_{nc,1}$  = partial pressure of the noncondensable component at initial conditions,  
 $P_{nc,2}$  = partial pressure of the noncondensable component at final conditions,  
 $V$  = vessel headspace volume,  
 $T$  = system temperature,  
 $R$  = is the Universal gas constant.

### **Heating Operations**

Emissions occur from heating operations. As the temperature in the vessel increases from an initial  $T_1$  to a final  $T_2$ , gases in the headspace leave the system through the process vent. If the heating takes place in a temperature range that is well below  $10^\circ\text{C}$  from the solvent boiling point then most of the emission occurs because of the effect that the temperature rise has on the molar capacity of the headspace. If the heating takes place within  $10^\circ\text{C}$  of the solvent boiling point then most of the emission occurs because of the effect that the temperature rise has on the solvent vapor pressure. This shift in the primary mechanism of the emission complicates the derivation of a mathematical solution. Equation (13) calculates the solvent emissions from heating as the difference between the moles of solvent that

vaporized into the headspace during the heating (first term) and the moles of solvent vapor that remained in the vessel at the conclusion of the heating (second term).

$$\text{Equation (13): } E_{n-i,out} = N_{avg} \ln \left( \frac{p_{nc,1}}{p_{nc,2}} \right) - (n_{i,2} - n_{i,1})_{vessel}$$

Where

$E_{n-i,out}$  = moles of volatile component i leaving the vessel,

$N_{avg}$  = average gas space molar volume during the heating,

$p_{nc,1}$  = partial pressure of the noncondensable component at T1,

$p_{nc,2}$  = partial pressure of the noncondensable component at T2,

$n_{i,1}$  = moles of condensable component in the vessel headspace at T1,

$n_{i,2}$  = moles of condensable component in the vessel headspace at T2.

## VENT DEVICES

### Single Stage Vent Devices: Condensers, Vacuum Pumps, and Vacuum Steam Jets

Depending upon processing and environmental needs, several devices are available to the chemical operator that can be installed in the process vent path.

Vacuum pumps and/or steam jets are a normal part of any process that operates under vacuum conditions. The boiling point temperature of any liquid is a function of the operating pressure. The lower the operating pressure, the lower the boiling point temperature that the liquid will exhibit. Therefore, distillation and evaporation operations can be performed at much lower temperatures when the process is operated under vacuum conditions. Lower operating temperatures enable the process to be run with higher product yields while at the same time fewer impurities in the process.

Vacuum pumps are mechanical devices that operate by way of an impeller or a set of veins that rotate at a high speed within a specially designed housing. Vacuum steam jets operate based on the venturi principle where steam or water is allowed to flow through a nozzle and into an expansion chamber of increasing cross sectional area. Vacuum is created by the negative change in fluid momentum.

A vent condenser is one of the most commonly used devices for recovering solvent from process vent gases while at the same time reducing air emissions. Vent condensers are normally installed in the vent path at a point which is nearest to the process. Solvent which has been recovered in this manner can be directly or indirectly recycled to the process. Therefore, vent condensers help the chemical operator to minimize the amount of fresh solvent that must be purchased for the facility.

During normal operation, single stage vent devices have an exit gas stream and an exit liquid stream. The term 'Single Stage' is used to describe the assumption that the exit liquid stream and the exit gas stream are in equilibrium while at the same time the material balance around the device is satisfied. In the case of a vent condenser, the exit liquid stream consists of condensate and the exit gas



stream consists of noncondensable components combined with any solvent vapors that did not condense at the operating temperature. In the case of a vacuum pump, the exit liquid stream consists of any working fluid (water, oil, ...) and dissolved components from the inlet process stream. The exit gas stream from the vacuum pump consists of noncondensable components (air, nitrogen, ...) combined with vapors from the working fluid and/or the process. In the case of the vacuum steam jet, the exit liquid stream consist steam condensate and dissolved components from the process. The exit gas stream from the vacuum steam jet consists of noncondensable components and residual vapors from the process and from the steam condensate.

When noncondensable gas components such as air or nitrogen are present in the inlet stream then the assumption is made that only a negligible quantity is soluble in the exit liquid stream and that 100% of the noncondensable component leaves the vent device by way of the exit gas stream. This assumption enables one to directly solve for the moles of noncondensable gas that are contained in the exit gas stream since they are equal to the moles that entered the vent device from the process.

If the inlet stream to a vent condenser contains only one condensable component and a noncondensable component then the solution to the equilibrium problem is readily found. The operating temperature and pressure of the vent condenser is known and the vapor pressure of the condensable compound can be calculated using the Clapeyron, Antoine, or comparable vapor pressure model. The emission rate of the condensable component from the vent condenser can be calculated by multiplying the moles of noncondensable component times the partial pressure ratio of the condensable component to the noncondensable component as shown in Equation (14). Three illustrations are provided in Section 4 of Chapter 16 that features a condenser with an inlet feed consisting of a single condensable component and noncondensable component nitrogen.

Equation (14): 
$$n_i = n_{nc} \frac{p_i}{p_{nc}}$$

Where

- $n_i$  = moles of condensable component i being emitted,
- $n_{nc}$  = moles of noncondensable component leaving the system,
- $p_i$  = partial pressure of condensable component i,
- $p_{nc}$  = partial pressure of the noncondensable component.

### **Rachford-Rice Method**

If the inlet stream from the process is free of noncondensable components (air or nitrogen) and it contains two or more condensable components then only the overall material balance around the vent condenser will be known. Equilibrium for the vent condenser calculated using the Rachford-Rice equation where component vapor pressures are calculated using the Newton convergence procedure. This might be the case for a partial condenser where the objective is to isolate and recover process material from highly volatile compounds. The resulting exit gas stream from the partial condenser might be sent to a thermal oxidizer for destruction. Section 4 presents one illustration where the Rachford-Rice equation is applied. Once Equation (15) has been solved by trial and error then the component material balance of the exit gas and liquid stream can be determined. The reader is referred to Section 4 of Chapter 16 for a more detail presentation of the Rachford-Rice solution procedures.

$$\text{Equation (15): } f\left(\frac{V}{F}\right) = \sum \frac{(K_i - 1) z_i}{1 + (K_i - 1) V / F} = 0$$

Where

- $K_i$  = ratio of the molar concentration of component  $i$  in the gas and liquid phases,
- $z_i$  = molar concentration of component  $i$  in the inlet feed stream,
- $V$  = moles of exit gas stream,
- $L$  = moles of exit liquid stream.

### **Modified Rachford-Rice Method**

For the typical vent device application, the inlet stream from the process contains a noncondensable component such as air or nitrogen and two or more condensable components. The presence of the noncondensable component in the system causes mathematical division by zero problems using the Rachford-Rice equation and so alternative methods to calculate a solution had to be developed.

The Rachford-Rice equation can be algebraically manipulated in such a way that the  $(K_i - 1)$  term becomes inverted as  $1/(K_i - 1)$ . The left side of Equation is used for the condensable components and the right side of Equation is used for noncondensable components. Equation (16) is solved in a similar manner as Equation (15) using the Newton convergence procedure.

$$\text{Equation (16): } f\left(\frac{V}{F}\right) = \sum_{i=1}^{C_c} \frac{z_i}{1/(K_i - 1) + V/F} + \sum_{j=1}^{C_{nc}} \frac{z_j}{V/F}$$

Where:

- $V$  = Exit moles of gas leaving the vent device,
- $F$  = Moles of feed to the vent device,
- $z_i$  = mole fraction of condensable component  $i$  in the feed stream,
- $z_j$  = mole fraction of noncondensable component  $i$  in the feed stream,
- $K_i$  = mole fraction of component  $i$  in the exit gas stream divided by the mole fraction component  $i$  in the exit liquid stream  $(y_i/x_i)$ .
- $C_c$  = number of condensable components in the system,
- $C_{nc}$  = number of noncondensable components in the system.

### **Partial Pressure Correction Method**

A second approach was developed for solving the multicomponent single stage equilibrium problems with noncondensable gases present. In the partial pressure correction method the moles of each condensable component are split between the exit liquid and gas phases as shown in Equation (17). 100% of the noncondensable component is assigned to the exit gas phase. The partial pressure of each

component is calculated from the molar composition of the gas phase using Dalton's Law and from the liquid phase using Raoult's Law (with activity coefficients if needed). The difference between the two partial pressures for each component is calculated in Equation (18). The fraction of each component in the liquid phase is adjusted using Newton-Raphson convergence until the two partial pressure calculations for each component agree as shown in Equation (17).

Equation (17):  $n_{i,F} = n_{i,L} + n_{i,V}$

Where:

- $n_{i,F}$  = moles of component  $i$  in the feed stream,
- $n_{i,L}$  = moles of component  $i$  in the exit liquid stream,
- $n_{i,V}$  = moles of component  $i$  in the exit gas stream.

Equation (18):  $f(n_i) = p_{i,L} - p_{i,V}$

Where:

- $p_{i,L}$  = partial pressure of component  $i$  calculated from the liquid stream,
- $p_{i,V}$  = partial pressure of component  $i$  calculated from the gas stream molar composition.

Equation (19):  $n_{i,L,k+1} = n_{i,L,k} - \frac{f(n_{i,k})}{f'(n_{i,k})}$

Where:

- $n_{i,L,k}$  = moles of component  $i$  in the exit liquid stream at iteration  $k$ ,
- $n_{i,L,k+1}$  = moles of component  $i$  in the exit liquid stream at iteration  $k + 1$ .

The partial pressure correction method is applied to several worked illustrations contained in the Chapter 16 document.

Illustration	Description
#4-6	Vent condenser featuring a miscible three component (methyl chloride, n-hexane, and toluene) condensate.
#4-10	Liquid-ring vacuum pump involving a single liquid phase multicomponent condensate. The liquid-ring vacuum pump uses water as a working fluid. Three miscible components from the process vent are processed through the pump. Portions of each component remain with the working fluid (water) and the remainder is emitted in the discharge air stream.

### **Material Balance Correction Method**

A third approach to the multicomponent single state equilibrium problem with noncondensable gases present is the material balance correction method. The moles of each condensable component are split between the exit liquid phase and the exit gas phase as shown in Equation (20). 100% of the noncondensable component is assigned to the exit gas phase. The partial pressure of each component is calculated from the liquid phase composition using Raoult's Law (with activity coefficients if needed). The moles of each condensable component in the gas phase are calculated from the moles and partial pressure of the noncondensable gas in the gas phase.

The moles in the liquid phase are added to the calculated number of moles in the gas phase for each component. The ratio  $\phi_i$  between the calculated total moles and the amount that entered the vent device is calculated for each condensable component, Equation (20).

$$\text{Equation (20): } \frac{n_{i,L} + n_{i,V}}{n_{i,F}} = \phi_i$$

Where:

- $n_{i,L}$  = moles of component  $i$  in the exit liquid stream,
- $n_{i,V}$  = moles of component  $i$  in the exit gas stream,
- $\phi_i$  = ratio of the calculated total moles and the moles entering the vent device for component  $i$ .

For component  $i$ , if the total calculated moles in the liquid and gas phases are greater than the amount in the inlet stream (  $\phi_i > 1.0$  ) then it implies that the moles of component  $i$  in the liquid phase is too high and need to be adjusted lower. On the other hand, if the calculated molar quantity of component  $i$  in the exit liquid and gas phases is less than the moles of  $i$  entering in the inlet feed stream (  $\phi_i < 1.0$  ) then it implies that the exit liquid stream does not contain enough of component  $i$  and that this amount should be increased as shown in Equation (21).

$$\text{Equation (21): } n_{i,L,k+1} = \frac{n_{i,L,k}}{\phi_{i,k}}$$

Where:

- $n_{i,L,k}$  = moles of component  $i$  in the exit liquid stream at iteration  $k$ ,
- $n_{i,L,k+1}$  = moles of component  $i$  in the exit liquid stream at iteration  $k+1$ ,
- $\phi_{i,k}$  = ratio of the calculated total moles and the moles entering the vent device for component  $i$  for iteration  $k$ .

The material balance correction method is applied to several worked illustrations contained in the Chapter 16 document showing its versatility.

Illustration	Description
#4-7	Vent condenser featuring a miscible three component (methyl chloride, n-hexane, and toluene) condensate.
#4-8	Vent condenser featuring a single liquid phase condensate with two component azeotrope (ethyl acetate and ethanol).
#4-9	Vent condenser involving a condensate with two immiscible liquid phases (toluene and water).

## CONCLUSION

In this article many of the key emission calculation models featured in EIIP Document *Chapter 16: Methods for Estimating Air Emissions from Chemical Manufacturing Facilities* have been reviewed. These basic rudimentary process models provide a foundation for assessing the air emissions that manufacturing operations across different industries have. A recently added section on single stage vent devices with worked illustrations has helped by providing mathematical procedures that can be used for calculating the air emissions from vent condensers, vacuum pumps, and vacuum steam jets.

From most of the emission calculation models it is easy to see how the quantity of VOC, HAP, and other compound emissions are related to the quantity of air or nitrogen that exits the process through equipment vents. Therefore, process changes that lead to reductions in air and nitrogen emissions would significantly impact the air pollution emissions from manufacturing operations. When single stage vent devices (vent condensers, liquid-ring vacuum pumps, or vacuum steam jets) are studied, it can be seen how the presence of air or nitrogen in the system greatly influence the capture efficiency of the condensable components. For example, if the inlet stream to a vent condenser contained no noncondensable components then the capture efficiency of the condenser would be 100% and there would be zero emissions. This is because air and/or nitrogen act as carrier gases and solvent vapors go along for the ride as shown in the ideal gas law relationship, Equation (7). Achieving this goal is not completely realistic but the importance of this cause and effect relationship provides insight that help engineers to design processes and facilities that are more air tight and provide greater operating efficiency.

It was also seen how the method that is used to introduce volatile components into a vessel can dramatically change the emission levels for the process. If the subsurface addition procedures are applied to the process instead of above surface addition procedures then the resulting air emissions would be significantly reduced. One illustration showed how the emissions of a VOC were reduced by approximately 70% simply because subsurface addition principles were used.

## REFERENCES

EPA, *Methods for Estimating Air Emissions From Chemical Manufacturing Facilities*, Volume II, Chapter 16, Section 4.2.3, EPA, Research Triangle Park, NC (Aug 2007).